Cruise: GU1702

Ship: R/V Gordon Gunter Expo Code: 33GG20170610 Dates: 06/10/2017 – 06/21/2017 Chief Scientist: Harvey Walsh

Equipment: Niskin bottle & Ship's Flow Thru (FT)

Total number of stations: 18

Location: U.S. Mid-Atlantic and New England coastal region

The samples were run as part of our coastal ocean acidification monitoring project.

Sample Collection

The discrete samples were collected from an old fashioned Niskin bottle triggered with a messenger onboard the R/V Gordon Gunter by H. Walsh and E. Broughton. Depths are approximate, there is no digital information about bottle trip depths. The date and time listed in the data file are UTC when each sample bottle was collected.

DIC:

18 locations, 20 samples each 500-ml, 2 duplicate samples.

Sample ID#: 90101, etc.; Station, cast number and Niskin bottle number

PI: Dr. Rik Wanninkhof

Analyzed by: Charles Featherstone and Patrick Mears

pH:

18 locations, 20 samples each 500-ml, 2 duplicate samples.

Sample ID#: 90101, etc.; Station, cast number and Niskin bottle number

PI: Dr. Rik Wanninkhof

Analyzed by: Charles Featherstone and Patrick Mears

TAlk:

18 locations, 20 samples each 500-ml, 2 duplicate samples.

Sample ID#: 90101, etc.; Station, cast number and Niskin bottle number

PI: Dr. Rik Wanninkhof

Analyzed by: Charles Featherstone and Patrick Mears

Sample Analysis

DIC:

Instrument	Date	Certified	CRM	CRM	Blank	Avg.
ID		CRM	Value	Offset	(Counts)	Sample
		(µmol/kg)	(µmol/kg)	(µmol/kg)		Analysis
						Time
AOML 3	09/28/2017	2017.95	2018.67	0.72	28.0	11
AOML 4	09/28/2017	2017.95	2010.87	7.07	28.0	20
AOML 4	09/28/2017	2017.95	2010.85	7.10	40.0	15

Analysis date: 09/28/2017

Coulometer used: DICE-CM5015- AOML 3

Blanks: 28.0 counts/min

CRM # 948 was used and with an assigned value of (includes both DIC and salinity):

Batch 153, c: 2017.95 µmol/kg, S: 33.357

CRM values measured: AOML 3: offset 0.72 µmol/kg (2018.67 µmol/kg). Average run time, minimum run time, maximum run time: 11, 8 and 14 min.

Analysis date: 09/28/2017

Coulometer used: DICE-CM5015- AOML 4

Blanks: 28.0 and 40.0 counts/min

CRM # 651 and 707 was used and with an assigned value of (includes both DIC and

salinity): Batch 153, c: 2017.95 µmol/kg, S: 33.357

CRM values measured: AOML 4: offset 7.07 and 7.10 μ mol/kg (2010.87 and 2010.85

umol/kg).

Average run time, minimum run time, maximum run time: 16, 8 and 20 min.

Reproducibility: (# samples and average difference): 2 duplicate samples were collected with an average difference $41.46 \, \mu \text{mol/kg} \, (5.07-88.00)$ and an average STDEV of $41.46 \, (3.59-62.22)$. The first sample for 440101 (1953.78) was marked as bad which resulted in such a large difference with its duplicate.

		DIC			
Instrument	Sample ID	(umol/kg)	Average	STDEV	Difference
AOML4	440101	1953.78			_
AOML4	440101	2041.78	1997.78	62.22	88.00
AOML4	970101	2054.92			
AOML4	970101	2059.99	2057.45	3.59	5.07
Average				41.46	41.46

CRM, salinity and HgCl2 correction applied: Salinity correction was applied using TSG salinity.

Remarks

The volume correction was applied due to added HgCl₂ (Measured DIC*1.00037). The first CRM of each cell was used for a CRM correction.

The DIC instruments were stable: the gas loop and CRM values did not change significantly throughout the life span of each cell.

The first sample for 440101 (1953.78) was marked as bad which resulted in such a large

difference with its duplicate.

The blank on AOML 3 (09/28/2017) was raised from 18.3 to 28.0 before running the CRM.

The blank on AOML 4 (09/28/2017) was raised from 21.2 to 28.0 before running the CRM. The blank was also raised again to 40.0 after running another CRM and before sample 13.

The samples were analyzed using the DICE (AOML 3 and 4) and a new coulometer from UIC, Inc. CM5015 with CM5011 emulation software.

pH:

Analysis date: 09/28/2017

Spectrophotometer used: HP Agilent 8453

Reproducibility: (# samples and average difference): 2 duplicate samples were collected with an average difference 0.0006 (0.0003 - 0.0009) and an average STDEV of 0.0004 (0.0002 - 0.0006).

System	Sample Bottle #	Sample ID	S	t	Corrected pH	Average	Difference	STDEV
HP Agilent	Dottie #	IIV						
8453	11	440101	35.07	19.743	8.0944			
HP Agilent								
8453	10	440101	35.07	19.788	8.0935	8.094	0.0009	0.0006
HP Agilent								
8453	17	970101	36.35	19.778	8.164			
HP Agilent								
8453	18	970101	36.35	19.762	8.164	8.164	0.0003	0.0002
Average							0.0006	0.0004

Temperatures measured during pH analysis

Sample ID	Station	Bottle #	Temperature Deg C
60101	6	1	19.742
180101	18	2	19.736
190000	0	19	19.756
190101	19	3	19.749
200000	0	20	19.760
260101	26	4	19.740
270101	27	5	19.746
330101	33	6	19.756

340101	34	7	19.769
420101	42	8	19.758
430101	43	9	19.767
440101	44	11	19.744
440101	44	10	19.778
530101	53	12	19.771
550101	55	13	19.777
830101	83	14	19.769
850101	85	15	19.783
930101	93	16	19.751
970101	97	17	19.742
970101	97	18	19.755

Remarks

The equations of Liu et al, 2011 formulated using the purified m-cresol purple indicator was used to determine pH of the samples. pH samples were analyzed at 20^oC at Full Scale (pH 0-14).

Samples were run on an automated system where the temperature was kept constant

Approximately 80 mL of sample was extracted from each DIC sample bottle by syringe before DIC analysis to determine the pH.

TAlk:

Analysis date: 10/17/2017

Titration system used: Open cell

CRM Batch 153, Salinity = 33.357, cert. TA = $2225.59 \mu mol/kg$.

On 10/17/2017 one CRM was analyzed before the samples and the same CRM was run at the end of analysis each day for each system.

The TA for the water samples was corrected using the daily averaged ratios between the certified and measured values of the CRMs run on each cell. The following table shows the CRM measurements for each day and cell.

Cell System	Date	Time	Bottle #	TA	\Delta CRM
1	10/17/2017	13:17:29	593	2222.72	
1	10/17/2017	21:33:19	593	2222.42	0.30
2	10/17/2017	13:39:01	683	2222.94	
2	10/17/2017	21:29:46	683	2223.37	0.43

Reproducibility: (# samples and average difference): 2 duplicate samples were collected with an average difference $4.10 \mu mol/kg (0.56 - 7.65)$ and an average STDEV of 2.90 (0.40 - 5.41).

System	Sample ID	TAlk	Average	Difference	STDEV
System 2	440101	2299.40	2299.12	0.56	0.40
System 2	440101	2298.84			
System 2	970101	2366.78	2370.60	7.65	5.41
System 2	970101	2374.43			
Average	_		_	4.10	2.90

Remarks

The CRM measurement for each day was used to correct the data for that day only. Both systems worked well.

Comments

The latitude, longitude, date, and time reported with the DIC, pH and TAlk measurements were taken from the sample field log. The field log values are provided for reference; no post-cruise assurance of accuracy has been done to this data.

The Sample ID is the sample station, cast number and Niskin bottle number for the discrete samples.

One of the samples from the flow-through line was considered bad and flagged 4 for DIC, TA and pH. This sample is not reported in the final data file.

Corresponding UW pCO2 data can be found at the following website http://www.aoml.noaa.gov/ocd/ocdweb/occ.html